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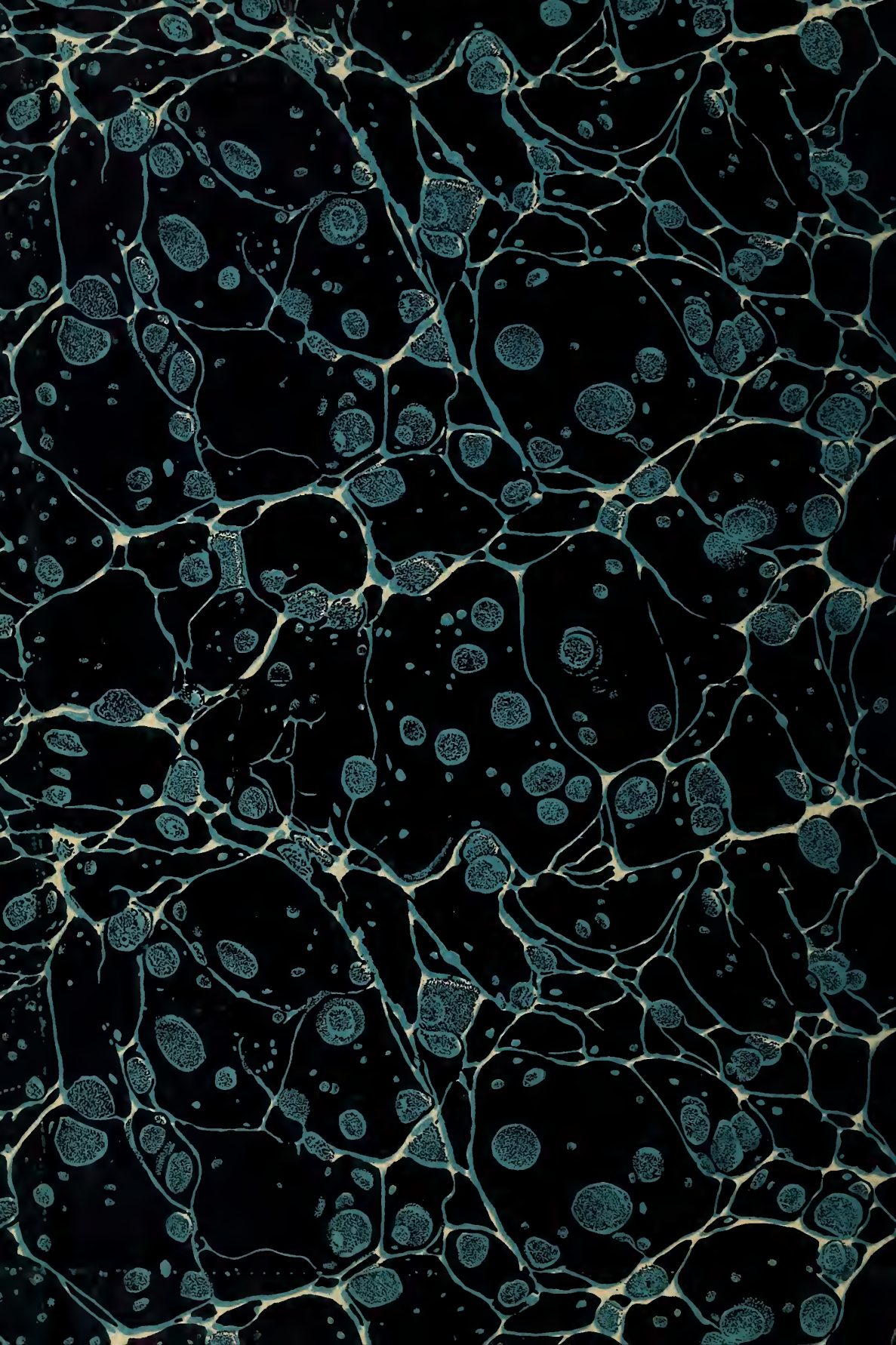

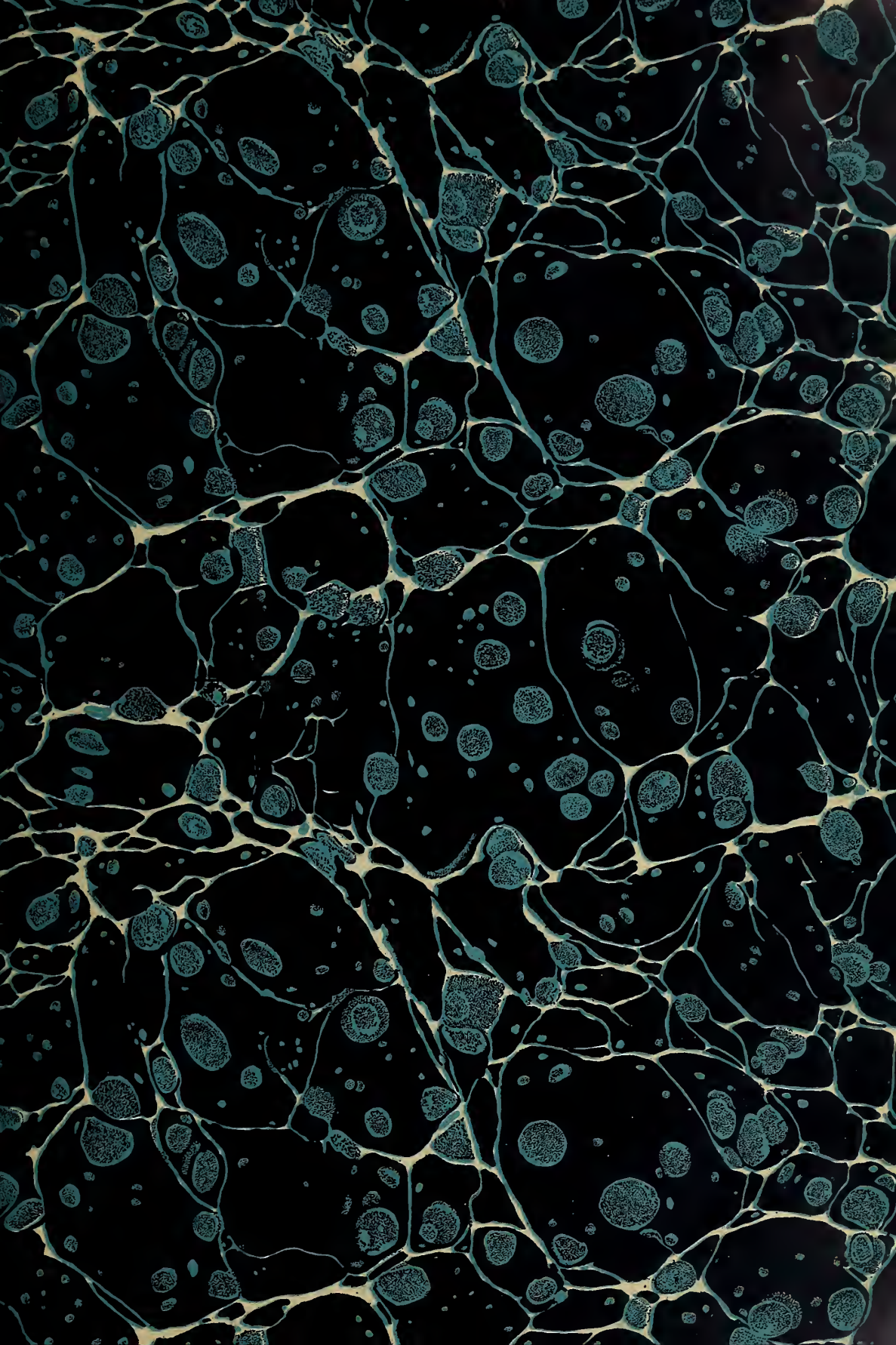

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BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 146

CADMIUM ELECTRODE FOR STORAGE-BATTERY TESTING

BY

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Bureau of Standards

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By H. D. Holler and J. M. Braham

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I. INTRODUCTION

In the operation and testing of storage cells it is frequently important, particularly in cases of low capacity, to know the individual potentials of the positive and negative plates of the cell. No standard method of measuring the potentials of storage-battery plates is recognized in the industry, but for many years the most common method has consisted simply in measuring, with an ordinary voltmeter, the potential difference between either plate of the cell and a piece of cadmium metal dipping into the electrolyte of the cell. Since the resistance of different voltmeters in common use varies over a wide range, it would not be surprising if different results were obtained with different voltmeters. Certain instances have been called to the authors' attention in which the sum of the cadmium-positive and cadmium-negative potentials is less than the cell voltage.

Since the Bureau of Standards requires for test purposes more accurate information about the reliability of this method, this investigation was undertaken to obtain experimental data which would give the information desired.

Several authors [1] have suggested the use of other electrodes for this purpose, viz, lead, lead peroxide, zinc, hydrogen, and the mercurous-sulphate electrode. The hydrogen electrode and mercurous-sulphate electrode are the most accurate and can be used in the laboratory, but are not well adapted to ordinary commercial testing. While any metal whose ions are harmless to the storage cell might be used, cadmium has been found by experience to be the most satisfactory.

II. SCOPE OF INVESTIGATION

In order to obtain definite information in regard to the conditions under which the cadmium electrode is used in present commercial practice, and to serve as a guide for our investigation, a letter was sent to a number of representative manufacturers of storage batteries asking the following questions:

1. What precautions are necessary in its use?
2. Can it be used with an ordinary voltmeter and what should be the resistance of the voltmeter?
3. Is it generally used to measure both plates or only one? Are its indications equally reliable for either plate?
4. What are the practical objections to its use?

Many of the manufacturers kindly replied to these questions. Their replies, for the most part, indicated that no special precautions were considered necessary, and no serious objections were offered to its use, but several of them said that interpretations of the results by inexperienced observers might be misleading. All agreed that the readings on both plates are equally reliable, but in some cases they said that only the potential of the positive is to be measured, from which the cell voltage is subtracted to give the potential of the negative plate. All, with one exception, agreed that any voltmeter of proper scale is satisfactory, the resistance of the instrument being considered of no importance.

It was necessary first to obtain an electrode as a standard with which a comparison of the cadmium electrodes could be made. The mercurous-sulphate half cell was adopted for this purpose. The reproducibility of the cadmium electrode was first determined and then the effect of temperature, drying of the electrode, and polarization of the electrode were studied. The reliability of the cadmium electrode for measuring the potentials of storage-battery plates during charge and discharge was also determined. The

[1] Trout, The Electrical News, **20**, p. 42; 1911. Jumau, L'Eclairage Electrique, **24**, p. 59; 1900. Jumau, Les Accumulateurs Electriques, p. 109; 1904. Liagre, L'Eclairage Electrique, **40**, p. 406; 1904.

most important part of the investigation proved to be the effect of polarization of the cadmium electrode upon the measurement of the potential of the positive plate.

The present investigation deals only with the accuracy of the cadmium electrode and does not discuss the cadmium readings with reference to the age or condition of the battery.

III. THE STANDARD ELECTRODE

As a standard electrode with which comparison of the cadmium electrode could be made a mercurous sulphate-sulphuric acid electrode of the form suggested by G. N. Lewis[2] was employed. The advantages of this electrode, aside from its high degree of reproducibility and constancy, is its common-ion constituency and the harmlessness of its components if introduced into the storage cell. For the precise measurement of potentials of storage-battery plates, the mercurous-sulphate electrode with a potentiometer is highly satisfactory and recommended for laboratory work, but not in commercial practice by ordinary operators.[3]

In order to minimize the liquid contact potential difference between the electrolyte of the storage cell and that of the half cell, the mercurous sulphate half cell was filled with pure sulphuric acid having a density of 1.250 at 25° C. The mercurous sulphate used was taken from a lot which had been specially prepared for use in the construction of Weston standard cells. Several of these half-cells were carefully prepared and checked against each other at frequent intervals of time. Variations in their values were negligible as compared with the differences in value of different cadmium electrodes under apparently identical conditions. All the results in this paper are referred to the mercurous-sulphate electrode containing sulphuric acid of density 1.250 at 25° C.

IV. REPRODUCIBILITY OF CADMIUM ELECTRODES

In order to determine the degree of uniformity of different cadmium electrodes, a number were prepared by sawing some of the ordinary cast metal sticks of about 0.75 cm in diameter into lengths of about 7.5 cm. These electrodes were introduced into sulphuric acid (sp. gr. 1.25) to a depth of about 2.5 cm and meas-

[2] Lewis, Jour. Am. Chem. Soc., 39, p. 2251; 1917.

[3] The mercurous-sulphate electrode is much more polarizable than the cadmium electrode. For instance, a resistance of 10 000 ohms in parallel with the potentiometer lowered the mercury potential 44 millivolts as compared with a lowering of the cadmium potential of only a few tenths of a millivolt.

urements with a potentiometer were made daily until consistent readings were obtained, which are given in Table 1. The electrodes, *L*, *M*, and *N* were heavily amalgamated, and *O* had been kept in acid for a month preceding this experiment.

It is to be noted that for two or three days after putting the electrodes into the acid, the potentials of different unamalgamated electrodes were different from each other by as much as 0.021 volt, for example, in the case of *D* and K, while the value of a given electrode was sometimes very erratic, for example, *K*. At the end of four or five days, after very marked corrosion was apparent, the values of different electrodes agreed within 0.01 volt.

As is evident in the case of *L*, *M*, and *N* the amalgamated electrodes exerted a potential less negative than that of pure cadmium, which is characteristic of cadmium amalgams.[4]

The variability of the values for freshly amalgamated cadmium is extreme as shown in Table 1 by the readings of *L*, *M*, and *N* on the first day. On the fourth day, however, corrosion had occurred to the extent that their values were in fair agreement. Presumably the gradually decreasing values on successive days are due to the formation of an increasing concentration of cadmium sulphate at the surface of the metal. From these observations it is evident that for satisfactory readings the cadmium electrode should be "aged" several days in battery acid until the surface of the metal is thoroughly corroded. Electrodes aged for several weeks gave the best results.

TABLE 1.—Reproducibility of Cadmium Electrode

[Electromotive Force (Volts) on Different Days]

Electrode	June 14	June 15	June 16	June 17
A	−1.108	−1.108	−1.103	−1.106
B	−1.103	−1.102	−1.105	−1.104
C	−1.109	−1.103	−1.108	−1.107
D	−1 101	−1.100	−1.100	−1.100
E	−1.105	−1.099	−1.102	−1.102
F	−1.105	−1.107	−1.106	−1.107
G	−1.114	−1.113	−1.111	−1.109
H	−1.112	−1.111	−1.109	−1.104
I	−1.111	[a] −1.101	−1.106	−1.106
J	−1.110	−1.100	−1.108	−1.109
K	[a] −1.122	[a] −1.093	−1.109	−1.108
L[b]	[a] −1.053	−1.094	−1.093	−1.092
M[b]	[a] −1.086	−1.100	−1.100	−1.098
N[b]	[a] −1.084	−1.101	−1.099	−1.095
O[c]	−1.110	−1.108	−1.105	−1.104

[4] Jaeger, Wied. Ann., 65, p. 106; 1898.

[a] Unsteady reading.

[b] Heavily amalgamated.

[c] Soaked in acid one month.

As indicative of the degree of constancy of a well-corroded electrode, which was initially slightly amalgamated, the following readings extending over a period of one month are given in Table 2:

TABLE 2

Date	Electromotive force (volts)	Date	Electromotive force (volts)	Date	Electromotive force (volts)
May 17	−1.097	May 29	−1.092	June 7	−1.100
May 19	−1.093	May 31	−1.095	June 16	−1.088
May 20	−1.091	June 2	−1.094	June 18	−1.096
May 21	−1.087	June 3	−1.083	June 19	−1.094

The maximum difference in the readings was 0.023, the difference between the minimum reading of —1.087 on May 21 and the maximum reading of —1.100 on June 7.

V. EFFECT OF TEMPERATURE

To determine the effect of change in temperature upon the potential of the cadmium electrode, the vessel holding the electrodes *I*, *J*, *K*, *M*, *N*, and *O* was set into a large oil bath, the temperature of which was slowly raised from room temperature (about 25° C) to about 40° C. (This range in temperature was taken as comparable with the maximum range in temperature of a storage battery in action.) It is sufficient to state that the maximum change in the average of the potentials of *I*, *J*, and *K* was only +0.0015 volt, and the corresponding change of *L*, *M*, and *N* was −0.0036 volt for a change in temperature of 15° C. Obviously the variation of potential due to temperature is negligible as compared with variations between different electrodes.

VI. EFFECT OF DRYING ELECTRODES

In the directions for the use of the cadmium electrode the precaution is usually emphasized that it is necessary to keep the electrode in "battery acid" so that it may be in proper condition for immediate use at any time. The importance of this point is illustrated by the following experiment, which was duplicated by several electrodes.

A well corroded cadmium electrode was removed from the acid and allowed to dry overnight. On the following morning it was returned to the acid and measurements in terms of the mercurous sulphate half-cell were immediately begun.

TABLE 3

Minutes after immersion in acid	Electromotive force (volts)	Minutes after immersion in acid	Electromotive force (volts)
0	−1.0855	10	−1.1035
2	−1.0884	27	−1.1064
7	−1.1011	40	−1.1066

The results in Table 3 show the necessity of soaking the electrode in acid for at least one-half hour before use, as otherwise an error of 0.02 volt may occur on this account.

VII. MEASUREMENT OF POTENTIALS OF STORAGE BATTERY PLATES

In connection with the testing of storage batteries at this Bureau both the cadmium electrode and mercurous-sulphate electrode were used for measuring the plate potentials during charge and discharge at different rates. From a large number of curves obtained two are given in Figs. 1 and 2 as typical ones.

The curves in Fig. 1 were obtained with a single storage cell charging at a constant current of 14 amperes which was about the 5-hour rate. The cadmium electrode used was similar to those already described and had been corroded in acid for several weeks. It was contained in a perforated glass tube to avoid any possibility of its touching the plates and extended vertically through the vent of the cell into the electrolyte about 2.5 cm. Any device of insulating material not attacked by the acid is suitable for eliminating any possibility of contact with the plates. During charge the density of the acid increased from 1.160 to 1.285.

The potentials of the positive and negative plates of the cell and of cadmium were all measured against the mercurous-sulphate electrode with a potentiometer. The mercury electrode has a very convenient potential value for such measurements since it lies about midway between the positive and negative plate, so that a reversal switch permits the quick setting of the potentiometer by a small adjustment. Since each division of the ordinate in Fig. 1 represents 0.01 volt, it is seen that the variation of the cadmium potential during the whole period of time is considerably less than 0.01 volt. It was more steady than expected, as the 14-ampere rate of charge was maintained throughout and the gassing was so vigorous as to expel part of the electrolyte.

The curves in Fig. 2 were obtained with a single storage cell discharging at 5 amperes, which was about the 5-hour rate and in the same manner as those in Fig. 1. During discharge the density of the acid decreased from 1.250 to 1.145. The variation of the cadmium electrode here is slightly less than in the case of

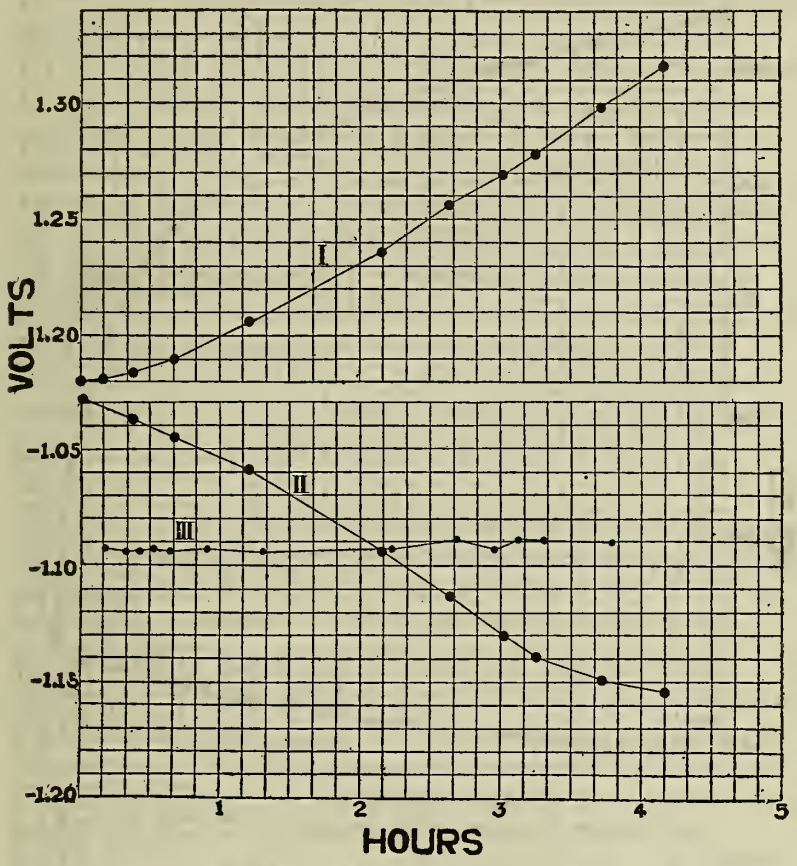

FIG. 1.—*Curve I represents the potential of the positive plate; Curve II, that of the negative plate; and Curve III that of a cadmium electrode, all measured against a mercurous sulphate electrode during the charge of the cell at a normal rate*

Fig. 1 and, in general, the readings during discharge were much more satisfactory than during charge.

It should be noted that the potential of the cadmium electrode in Fig. 1 is about 0.01 volt more negative than it is in Fig. 2. This difference represents approximately the variation to be expected of the cadmium electrode.

VIII. POLARIZATION OF CADMIUM ELECTRODE

1. GENERAL

From the curves in Figs. 1 and 2 it is clear that the cadmium electrode is constant for several hours within about 0.01 volt when

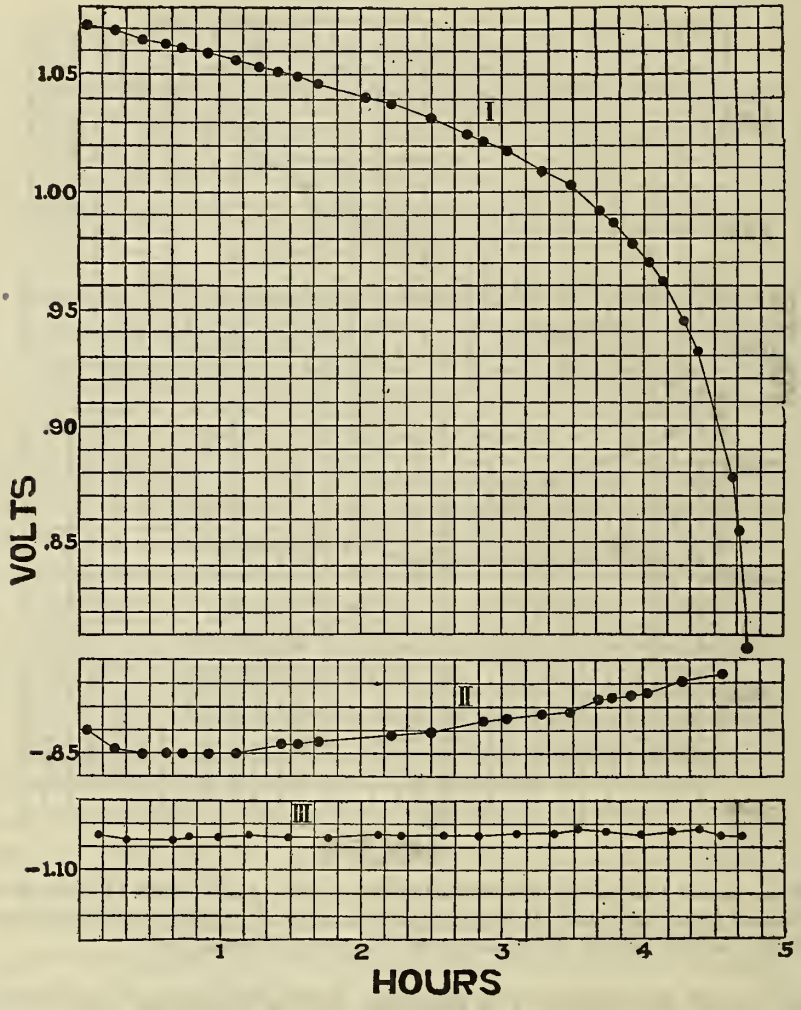

FIG. 2.—*Curve I represents the potential of the positive plate; Curve II, that of the negative plate; and Curve III, that of a cadmium electrode, all measured against a mercurous sulphate electrode during discharge of the cell at a normal rate*

the measurements are made with a potentiometer. Since, however, in commercial practice a voltmeter having a resistance of only 200 or 300 ohms is ordinarily used, it was important to determine whether the currents drawn by such an instrument

produce appreciable polarization of the cadmium electrode. For instance, in Figs. 1 or 2, if the cadmium electrode were polarized when used for making the measurements, the curve for the positive plate *I* would be too low and that for the negative plate *II* would be too high by an amount equal to the polarization of the cadmium electrode, the polarization of the plates of the cell being considered negligible.

Polarization increases with the current density on the surface of an electrode. Since the potential of the positive plate with reference to the cadmium electrode is many times that of the negative plate, the current flowing through the voltmeter when the positive plate is being measured is proportionately larger than the current flowing when the negative plate is measured. The error due to polarization in measuring the positive plate should, therefore, be much greater than for the negative plate, when a voltmeter of the same resistance is employed.

Since the current density is inversely proportional to the area of the electrode, the polarization and therefore the error in measurement should be expected to be greater the smaller the electrode used.

Although a considerable number of electrodes of different forms and sizes were tried out, the results of only a few are here given as representative of the results obtained. All electrodes were thoroughly corroded in acid before use and some were inclosed in hard-rubber cases, glass tubes, and rubber tubing, but these devices had no effect upon the readings obtained, their only advantage being protection against possible contact with the plates of the battery. Any kind of an inert insulator is equally satisfactory. The use of a porous porcelain cup was tried with the idea that the potential of the cadmium would be less affected by convection currrents. It, however, was no more nearly constant than a bare electrode

2. METHOD OF MEASUREMENT

The procedure employed for measuring polarization consisted simply in making a first reading of the potential of the battery plate against the cadmium electrode with a potentiometer, and then a second reading with the selected resistance in parallel with the potentiometer. The difference in the two readings is the polarization produced by the current flowing through the known resistance. The results are given in curves of Fig. 3, polarization being expressed in millivolts, for the resistances used, which were

varied from 250 to 10 000 ohms. The lower resistance (250 ohms) probably represents the resistance of the average voltmeter used in practice for such measurements. The upper resistance (10 000 ohms) represents approximately the minimum resistance which may be used without causing perceptible polarization of the cadmium electrode when measuring the positive plate.

3. EFFECT OF SIZE AND SHAPE

Representative types of electrodes used are given in Table 4.

TABLE 4

Number	Type	Diameter	Depth in acid	Area of contact
		Mm	Mm	Cm^2
E1	Rod	7.5	20	5.2
E8	do	4	25	3.3
E5	do	2	25	1.6
E3	Disk	12.5	25	6.4
E6	do	17	25	8.8

Of the electrodes listed in Table 4, E1 was least polarized. The polarization of E1, when used for measuring the positive plate, is given in Fig. 3 by curve *II*, and for the negative plate by curve *IV*. Thus, with a resistance of 250 ohms, the polarization was about 33 millivolts when measuring the cadmium-positive potential of 2.176 volts, and about 2.5 millivolts when measuring the cadmium-negative potential of 0.149 volts. The ratio of the two polarization values $\frac{33}{2.5}$ $(=13)$ is approximately equal to the ratio of the two potential values $\frac{2.176}{0.149}$ $(=14)$; that is, the polarization of the cadmium electrode is directly proportional to the potential being measured.

Electrode E3 was most polarized of any electrode in Table 4. Curve *I* in Fig 3 represents the cadmium-positive potential of electrode E3 and curve *III* the cadmium-negative potential. The ratio of the polarization values in this case is $\frac{108.4}{7.6}$ $(=14.3)$.

The polarization values of the electrodes listed lie between the values for E1 and E3. Although the calculated area of E3 is slightly greater than that of E1, the polarization is greater. This is probably due to the difference in their states of corrosion which might produce a greater difference in their active surfaces than is indicated by their areas as calculated from their dimensions.

Similarly, although electrode E5 had about one-half the area of E8 their polarization values were about equal. Here also the state of corrosion was probably the determining factor.

4. EFFECT OF DEPTH IN ELECTROLYTE

All measurements expressed in Fig. 3 were made upon electrodes immersed in the electrolyte 20 to 25 mm. Experiments were made

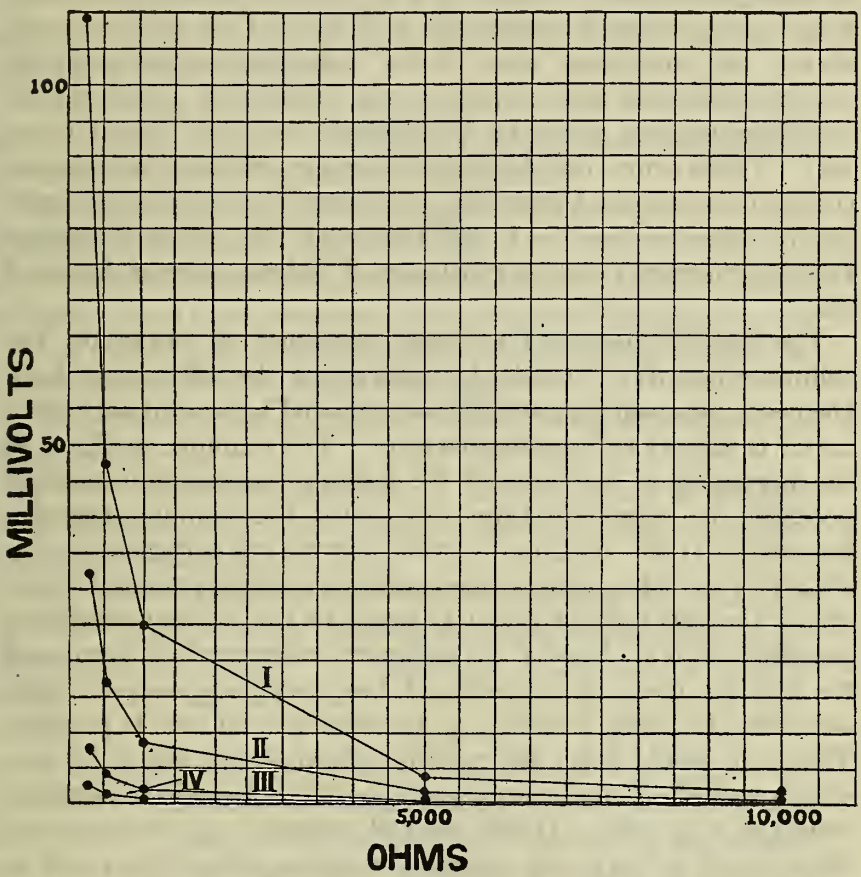

FIG. 3.—*Curves I and II represent the maximum and minimum values of the polarization of cadmium electrodes when used for measuring the potential of the positive plate with different resistances in parallel with the potentiometer. Curves III and IV represent the corresponding polarizations for the same cadmium electrodes when used for measuring the potential of the negative plate. For further explanation see p. 12.*

to determine the polarization of the electrodes at less depths. When the depth was decreased to 5 mm the polarization of E1 with 1000 ohms was increased from 5.4 to 8.9 millivolts. For E6 under the same conditions the polarization value changed from 4.9 to 29.5 millivolts.

The changes in polarization values of the other electrodes were between the values given for E1 and E6. It is obvious, therefore, that the electrode should extend into the electrolyte to the maximum depth possible.

5. SIGNIFICANCE OF POLARIZATION ERROR

The errors due to polarization are significant as shown by the following discussion. Thus, in Fig.3, when the parallel resistance is 250 ohms which is comparable with that of an ordinary voltmeter, the maximum error of the cadmium-positive potential measurement was 0.11 volt, and the maximum error of the cadmium-negative potential measurment was only about 0.008 volt. These errors due to polarization are probably representative of those in usual practice. To reduce the polarization error in the cadmium positive to less than 0.01 volt, curve *I* requires that the voltmeter have a resistance of, at least, several thousand ohms.

The method employed by some operators of obtaining the cadmium-negative potential by subtracting the cell voltage from the cadmium-positive potential as measured by an ordinary voltmeter is subject to considerable error. For example, in Fig. 2 at the beginning of discharge of the battery the cadmium-positive potential is (1.07 + 1.08) or 2.15 volts; the cadmium-negative potential is (1.08 − 0.84) or 0.24 volt; and the cell voltage is (1.07 + 0.84) or 1.91 volts; that is, the cadmium-positive potential (2.15) minus the cell voltage (1.91) is equal to the cadmium-negative potential (0.24). Now, if an ordinary voltmeter had been used for making the measurements of the cadmium-positive value, according to curve *I* in Fig. 3, an error of 0.10 volt is possible. This error would lower the position of curve *I* in Fig. 2 by 0.10 volt (10 divisions on the scale) and the cadmium-positive potential would be 2.05 volts. If now the cell voltage (1.91) is subtracted from (2.05), we have the cadmium-negative value of 0.14 volt as compared with the true value of 0.24 volt. From the curve *II* in Fig. 2 it is evident that the error of such a method of measurement is much larger than the total change in the potential during discharge.

The following procedure is suggested by which it is possible to avoid the errors described above. According to curves *III* and *IV* in Fig. 3, the error in measuring the cadmium-negative potential is very small, less than 0.01 volt, when a 250-ohm voltmeter is used. If, therefore, the cell voltage is added to the cadmium-

negative potential, the error due to polarization in measuring the cadmium-positive potential is avoided. This procedure does not permit a check upon the readings, but is free from the usual error of the cadmium-positive measurement.

IX. CONCLUSIONS

1. The cadmium electrode is accurate to about 0.02 volt provided the proper precautions are taken. It was found to be constant within 0.01 volt during several hours, but from day to day it varied as much as 0.02 volt.

2. The cadmium electrode should be corroded several days in acid, a thorough state of corrosion being of greater importance than the exact size and shape of the electrode.

3. Amalgamation is not recommended since it makes the potential less negative and of uncertain value.

4. In case the surface of the electrode is allowed to dry, it should be soaked in acid for at least one-half hour before being used.

5. The depth of immersion should be made as great as possible, by adding electrolyte to the cell if necessary.

6. More steady readings are obtainable during discharge than during charge.

7. For accurate measurements of the potentials of storage-battery plates, the mercurous-sulphate electrode with a potentiometer is recommended.

8. The error in measurement with the cadmium electrode due to polarization is in many cases large, being proportional to the potential being measured. It is therefore many times greater in the case of the cadmium-positive than of the cadmium-negative potential.

9. The greatest error in the use of the cadmium electrode is due to polarization caused by a voltmeter of low resistence. Obviously this error may be avoided by using an instrument having a resistance of several thousand ohms. In case a voltmeter of low resistance must be used, the best procedure is to measure the cadmium-negative potential to which the cell voltage may be added to obtain the cadmium-positive potential. If a check upon the readings is required, then either a potentiometer or a high-resistance voltmeter is necessary.

WASHINGTON, August 4, 1919.